11.—ANALYSIS OF SOIL COLLOIDS BY X-RAY DIFFRACTION METHODS.

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CONTENTS.

I. INTRODUCTION.

In 1916 Debye and Scherrer in Germany and Hull in America developed a method (termed the powder method) of investigating the crystal structure of crystalline material in the form of powder. If a monochromatic beam of X-rays defined by pin-holes is directed on to a small rod of the powder in a suitable container, diffraction lines in the nature of a "spectrum" appear on a cylindrical photographic film concentric with the powder. These diffracted lines are the intersections with the film of cones of rays diffracted from the powder, each cone being characterised by a semi-vertical angle of $2\theta_{hkl}$[†] where θ_{hkl} is defined by Bragg's equation $n\lambda = 2d_{hkl} \sin \theta_{hkl}$. A particular crystalline material is characterised by a particular distribution of lines and of line intensities in its "spectrum" or X-ray diffraction pattern. The components of a mixture of crystalline materials may be recognised if the pattern of each component in the composite pattern can be identified. Colloidal particles greater than about 0.1μ may be sufficiently crystalline to react in this way and so a mixture may be analysed into its components. A decade or more ago attempts were first made by workers in Europe and America to apply this powder method to the investigation of the colloidal clay content of soils.

In this paper the authors give an account of a technique developed in general for the investigation of crystalline material in powdered form and in particular for the investigation of soil colloids. An account is also given of results obtained for two local soil samples.

The clay samples investigated were supplied by the State Department of Agriculture through Dr. Teakle, whose enthusiasm first aroused the interest of the senior author in this work. Mr. G. H. Burvill, Agricultural Adviser to the State Department of Agriculture, was responsible for the actual separation of the clays.

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† See, for example, W. H. and W. L. Bragg, " The Crystalline State," Chapters III. and IV.

II. MATERIALS.

The following particulars with regard to the location of the profile from which the soil samples were obtained, the method of separation of the clay fractions and analytical data with respect to soil samples and clay samples were kindly supplied by Mr. Burvill.

A. *Location.*

The two samples supplied (A1346 and A1351) represent the subsoil (6 inches–30 inches) and deep subsoil (120 inches–144 inches) respectively, in a profile of the soil type *Circle Valley* sand taken at Red Lake (longitude 121° 45′ E. ; latitude 33° 08′ S.) in the Salmon Gums district. They are typical of the subsoil and deep subsoil conditions over large areas in that district.

B. *Method of Separation.*

The clay separations followed in general the methods adopted in the procedure for mechanical analysis by the pipette method as described in C.S.I.R. (Aust.) Pamphlets Nos. 8 and 13, with the following variations :—

(i) To avoid chemical changes the hydrogen peroxide treatment and the acid treatment were dispensed with. The omission of the former is presumed to be of little consequence as the organic content is very low.

(ii) From each soil sample two clay samples were prepared in one of which dispersion was made in distilled water ; in the other caustic soda was used. Thus four clay samples in all were supplied.

(iii) Care was taken to avoid any heat treatment at any stage in the process. The clay was separated from the suspension by flocculation with calcium chloride, filtration, washing twice with 95% alcohol and air-drying.

The clay samples so prepared should contain most of the particles less than 2μ in effective diameter. The colour of A1346 is greyish yellow ; that of A1351 pinkish brown.

C. *Analytical Data relating to Soil Samples.**
1. *Mechanical and Chemical Data.*

	A 1346	A 1351
Depth of sample (in inches)	6–30	120–144
	per cent.	per cent.
Coarse sand (2·0–0·2 mm.)	10·7	11·3
Fine sand (0·2–0·02 mm.)	26·1	28·1
Silt (0·02–0·002 mm.)	3·0	1·1
Clay (less than 0·002 mm.)	51·5	52·8
Loss on acid treatment	5·3	2·0
Moisture	6·1	7·0
Loss on ignition	7·0	5·4
Calcium Carbonate	3·6	*nil*
Total water soluble salts	0·679	1·216
Sodium Chloride	0·546	0·923
Soluble in Hydrochloric Acid—		
Lime (CaO)	1·603	0·011
Magnesia (MgO)	1·481	0·608
Potash (K_2O)	1·625	1·328
Soda (Na_2O)	0·646	0·719
Reaction (pH)	8·58	4·38

*Received from the Department of Agriculture and shortly to be published by G. H. Burvill, B. L. Southern and L. J. H. Teakle.

2. *Exchangeable Cations, excluding Hydrogen.*

Soil.	Total m.e. per 100 gms. of Soil.	Per cent. of total bases.			
		Ca.	Mg.	K.	Na.
A 1346	27·17	12	40	13	35
A 1351	18·23	0	47	10	43

3. *Chemical Analysis of Clay Fractions.*

——	SiO_2	Al_2O_3	Fe_2O_3	SiO_2/R_2O_3
	%	%	%	
A 1346	47·92	22·99	10·33	2·75
A 1351	47·84	21·12	12·32	2·80

III. EXPERIMENTAL DETAILS.

X-Ray Unit and Radiation.—A Hilger-Mueller Improved X-ray gonio-meter spectrograph was used, with certain modifications alluded to below. Radiation was supplied by a Hilger all-steel gas X-ray tube energised by a 16 inch Victor induction coil with mercury make and break. In the case of the four clay samples exposures were obtained with filtered Cu radiation. In the case of the two samples of A1346 and the caustic soda dispersed sample of A1351, Fe radiation was also used. β lines appearing in a diffraction pattern obtained with unfiltered radiation may readily be identified by comparison with a pattern that has been obtained with filtered radiation.

Ni Filter and Method of Preparation.—The Cu radiation was rendered monochromatic by means of a 10μ Ni filter. This filter served as a window for the X-ray tube throughout the course of the work. Its thickness was not sufficient to suppress the Cu $K\beta$ radiation in the case of heavily exposed lines, but as this occasioned no difficulty, the 10μ filter was retained with a view to avoiding unnecessary loss of intensity.

It was found that a satisfactory way of preparing Ni foil of any desirable thickness was to deposit the foil electrolytically on a cathode consisting of a stainless steel button set in copper. Since the Ni film will not adhere to stainless steel, the portion overlying the button can readily be removed.

Collimation.—The X-ray beam was collimated by a long cylindrical channel, the diameter of which at each end was limited by two short cylindrical stops fitting into the channel. Each stop was of total length (including a collar) of 1·5 cm., and the total length of the collimating system was 6·2 cm. The diameter of the stops used in the course of this work was 0·5 mm. The powder preparation was mounted at a distance of 0·4 cm. from the near end of the collimating system and 8·6 cm. from the window of the tube. This method of collimation, which involved a modification in the design of the original unit, was adopted after trial of other methods. At 2·8 cm. from the preparation the direct beam so collimated was about 0·7 mm. wide and about 1·2 mm. high.

Mounting of Powder.—The clay fractions were held in small celluloid containers of internal diameter not exceeding 0·35 mm. and of wall thickness approximately 0·1 mm. To make these containers, short straight lengths of

copper wire of diameter 0·32 mm. were coated with a smear of specially selected candle-grease and dipped into a solution of celluloid dissolved in acetone. When the acetone had evaporated, leaving a thin precipitate of celluloid on the wire, it was held in steam and the wire gently withdrawn. The powder was introduced with the help of a fine brush and a fine glass rod.

The preparation was adjusted so as to remain in the X-ray beam upon rotation. A method of mounting was developed which made it possible to change from one preparation to another with very little re-adjustment. In the course of the exposure, in order to ensure an accurately fixed mean position of the powder relative to the cylindrical photographic film, the preparation was continuously rotated by clockwork.

Mounting of Films.—Ilford double-coated X-ray film was used, in all cases backed by Levy-West Fluorazure intensifying screen. The screen was cut to size, shellaced along the cut edges and, to prevent the formation of creases, bent into the shape of the camera after the shellac was thoroughly dry. The film and intensifying screen were carried in specially designed black paper envelopes.

The cylindrical camera used had a radius of approximately 2·8 cm. Other cameras available have a radius of 4·3 cm. and 5·6 cm. respectively. The envelope and its contents were held in position by means of two metal bands (which held the envelope pressed against the camera), one at the top and one at the bottom. Additional clamping was provided for the one at the top by means of three small brass clamps.

Exposure Times, and Choice of Radiation.—Under normal operating conditions of 4 mA and about 60 K.V.P. suitable exposures were obtained in at most two hours with Cu Kα radiation. The photographs of the clay fractions so obtained, when compared with photographs of a pure substance (*e.g.*, KCl), showed a pronounced general scattering. As the scattering of the Cu radiation by the Fe present in the sample could explain this effect, photographs were taken with Fe radiation, but no marked improvement was observed. This change of radiation involved much longer exposure times. It appeared that factors such as the presence of amorphous material and the size of the particles were responsible for the scattered background. The insertion of Cu foil or Al foil in front of the film failed to improve the contrast.

Absorption of Direct Beam.—The direct beam was absorbed in a small rectangular chamber mounted in front of the film. The dimensions of the chamber (which was designed to replace the larger one supplied with the instrument) were made such that when it was placed close up to the film mounted in the smallest camera (radius 2·8 cm.), an X-ray shadow of approximately 3·5 mm. wide was obtained. A diffraction ring of this diameter corresponds to a spacing (d/n) of 25 A (with Cu Kα). The prominent montmorillonite spacing at 15 A could readily be recorded. This method of dealing with the direct beam was selected, as a result of experiment, in preference to the method of allowing the beam to pass out through a hole in the film.

Heat Treatment.—In view of the observations of other workers that the basal spacing of montmorillonite varies with the water content, and that the kaolinite pattern is destroyed at 500° C, provision was made for heating the colloid material in air in an electric furnace.

IV. DETERMINATION OF d/n BY A GRAPHICAL METHOD, AND ACCURACY OF RESULTS.

X-radiation of wave-length λ is reflected from a given set (hkl) of crysta lattice planes with interplaning spacing d_{hkl} at a glancing angle θ_{hkl} defined by Bragg's equation. Under the conditions of the powder method, these rays constitute a cone and all the possible (hkl) sets of lattice planes will give rise to the family of cones referred to in the introduction. The trace on the cylindrical film of any one of these cones is two symmetrical curved lines approximately arcs of a circle whose centre is the point where the direct beam leaves the camera. (In the case of a cone with semi-vertical angle greater than 90° the centre of the arcs is the point where the direct beam enters the camera). The Bragg angle θ may be deduced from a measurement of the maximum separation (2s) of these two arcs (the measurement being made along the film in the equatorial plane) and from the relation $\theta = s/2r$, where r is the radius of curvature of the film. (In the case of a cone with semi-vertical angle greater than 90°, 2s is the minimum separation).

A graphical method was devised for determining d_{hkl}/n from measurements of the corresponding 2s. Dropping subscripts we have from Bragg's relation—

$$(d/n) \sin \theta = \lambda/2.$$

Expanding $\sin \theta$:
$$(d/n)\ (\theta - \theta^3/3! + \theta^5/5! - \ldots) = \lambda/2.$$

Substituting $\theta = s/2r$:
$$(d/n)\ [s/2r - (s/2r)^3/3! + (s/2r)^5/5! - \ldots] = \lambda/2.$$

Therefore :
$$(d/n)\ (s/2r)\ [1 - s^2/24r^2 + s^4/1920r^4 - \ldots] = \lambda/2 ;$$
and, finally,
$$(d/n)\ 2s\ [1 - (2s)^2/96r^2 + (2s)^4/30720r^4 - (2s)^6/20643840r^6 + \ldots] = 2\lambda r.$$

Taking logs we get, if r is constant :
$$\log (d/n) + \log 2s\ [1 - (2s)^2/96r^2 + \ldots] = \text{constant}$$
where the constant is $\log 2\lambda r$.

Write this :
$$\log (d/n) + \log f(2s) = \text{constant}.$$

A graph of $\log (d/n)$ plotted against $\log f(2s)$ will therefore be a straight line with gradient −1. If r varies $f(2s)$ is a function of r and the value of r in each term of $f(2s)$ that contains r will be the value appropriate to that particular value of 2s. If the variations are small, $f(2s)$ is independent of r to the second order of small quantities. The form of the graph will depend upon the way in which r varies along the film.

From a powder photograph taken with a standard crystalline substance (K Cl) and Cu K α radiation, values of r for the smallest camera were calculated by direct application of Bragg's equation. 6·277 A was adopted as the edge of the unit cell of K Cl and 1·539 A as the wave-length of Cu K α. These values of r were found to vary uniformly along the film. In view of these variations and since the minimum value of 2s occurring in the K Cl diffraction pattern taken under these conditions is about 2·8 cm., Mo K radiation was substituted for Cu K α and another K Cl photograph taken in order to record

lines nearer the direct beam and so to extend the range of calculated r's. The total variation in r is small. It was apparent, however, since r could be calculated over a range of $2s$ common to both films that r varied from film to film. This variation from film to film was small ; no means was devised of eliminating it. A mean value of $2 \cdot 80$ cm. for r (allowing for variations along a film and from film to film) was adopted. It was found that this mean differed by less than 2% from any radius on any film within the range of $2s$ recorded on the clay films.

This mean value of r was used in evaluating log $f(2s)$, and the graph of log (d/n) and log $f(2s)$ was plotted for the K Cl powder photograph taken with Cu radiation. Values of log $f(2s)$ obtained from the Mo photograph and corresponding values of log $[(d/n)(\lambda_{Cu}/\lambda_{Mo})]$ were also plotted. $[(d/n)(\lambda_{Cu}/\lambda_{Mo})]$ is the value of d/n (fictitious) corresponding to a line (produced by Cu radiation) with the same $2s$ as a K Cl line produced by Mo radiation. $\lambda_{Cu}/\lambda_{Mo}$ was adopted as $2 \cdot 167$. The two graphs were linear but, in view of the variation of radius from film to film, not exactly collinear.

A mean graph was adopted as the final graph. In the case of an unknown line the procedure was to measure $2s$, calculate $f(2s)$ and from this graph to deduce d/n.

This graph applies to a film of mean radius of $2 \cdot 80$ cm. The approximately uniform variations of r along the film are taken into account in this graph except in so far as $f(2s)$ is in reality a function of r. The adoption of a fixed value for r ($2 \cdot 80$ cm.) involves for a 2% variation in r referred to above, an error of from 2% to $1\frac{1}{2}$% in the value of any d/n deduced from the graph over the range 10 A to 1 A.

The K Cl lines were sharp and the background relatively clear. The soil colloid lines were fairly diffuse and the scattered background fairly intense. Optical methods of measuring $2s$ were unsatisfactory. A calibrated transparent millimetre scale was used for all but the very faintest lines ; in their case a metal scale was used. Measurements of $2s$ were made independently by both authors. For all but the faintest lines the maximum error in measuring $2s$ was considered to be $0 \cdot 1$ mm. This corresponds, over a range of d/n from 10 A to 1 A, to a range of error in d/n from 1% to zero respectively. For the very faintest lines the maximum error is larger.

Due therefore to variations in r and errors in $2s$ the total maximum percentage error in the case of all but the faintest lines varies from 3% in the vicinity of 10 A spacings to $1\frac{1}{2}$% in the vicinity of 1 A spacings.

On some of the K Cl films taken with Cu Kα radiation the diffraction lines did not always appear simple. Some of the lines were accompanied by a faint satellite. The separation of the two was generally too large for the effect to be attributed to the α_1 and α_2 components and much too small to be attributed to the α and β components. It was not the same on different films on which the effect was observed, and moreover the effect appeared only with lines of large curvature. The satellite was always on the same side of the line as the centre of curvature. By suitable choice of film no error, it is believed, has been introduced by this effect. No explanation of the effect has been found.*

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*The observed effect (at least as far as the inner lines are concerned) may be attributed to absorption of the radiation by the powder material (as suggested, in correspondence, by Dr. G. Nagelschmidt of the Rothamsted Experimental Station).

V. MEASURED SPACINGS AND INTENSITIES, WITH COMMENTS.

The value of d/n for every observable line in the powder photographs of the water dispersed sample of A 1351 (Cu radiation) and in the caustic soda dispersed sample of A 1351 (Cu radiation and Fe radiation) was deduced from the graph. In the case of the observed values of $2s$ on films obtained with Fe radiation, the graph gave $[(d/n)(\lambda_{Cu}/\lambda_{Fe})]$. d/n was therefore obtained by multiplying this quantity by $\lambda_{Fe}/\lambda_{Cu}$. The value adopted for this ratio was 1·257.

Powder photographs of the samples of A 1346 (water dispersed and caustic soda dispersed) taken with Cu radiation and with Fe radiation appeared to be identical (both with respect to spacings and with respect to line intensities) with corresponding photographs of the A 1351 samples. Measurements of $2s$ confirmed this. Values of d/n were not deduced.

In Table (1) are tabulated all observed values of d/n for the clay samples of A 1351. Intensities are estimated visually.

TABLE (1).

Interplanar Spacings of A 1351.

Line.	Intensity.	Water dispersed. Cu radiation.	Caustic Soda dispersed. Cu radiation.	Fe radiation.
1	m	10·27 A	10·15 A	10·44 A
2	m	7·26	7·26	7·12
3	v w	...	...	5·82
4	v w	4·97	4·97	4·91
5	v s	4·47	4·46	4·45
6	v w	4·17	...	...
7	m	3·56	3·56	3·54
8	m	3·31	3·31	3·33
9	w	...	3·03	3·02
10	w	2·86	2·84	2·82
11	s	2·57	2·56	2·56
12	d	2·39	2·41	2·38
13	v w	2·16	2·10 {	2·20 / 2·08
14	v w	1·97	1·97	1·97
15	v w	1·84	1·88	1·84
16	d	} 1·66	1·66 {	1·68
17	d	/		1·64
18	s	1·49	1·49	1·48
19	v w	1·44	...	1·42
20	v w	1·36	1·36	1·36
21	w	1·29	1·29	1·29
22	w	1·24	1·23	1·24

v s = very strong ; s = strong ; m = medium ; w = weak ; v w = very weak ; d = diffuse.

With regard to the use of Fe radiation, a definite resolution into two lines (16 and 17) was observed of what appears with Cu radiation to be one broad diffuse line. A doubtful resolution of line 13 was also observed (admitted by one observer only). Similar differences were observed with A 1346. Line 3 appears only with Fe radiation and (taking into account A 1346 and A 1351) with both water dispersed and caustic soda dispersed material. This

line (which is extremely faint) has not been indentified.   Reference has already been made to the similarity of scattered background with both types of radiation.

The only observed difference between water dispersed and caustic soda dispersed material is in the case of A 1346 a reversal of intensity of lines 9 and 10.   In the water dispersed material line 10 is more intense than line 9 ; for the caustic soda dispersed material the reverse is true.   In A 1351 line 9 is absent in the water dispersed material and of similar intensity to line 10 in the caustic soda dispersed material.   It appears that the effect of caustic soda treatment is to increase the intensity of line 9.   This line (as will be seen in section VI) is attributable to a mica mineral.

VI. ANALYSIS OF X-RAY DATA.

The X-ray diffraction patterns of clay minerals are very much alike. The clay minerals however can be divided into three groups which can be fairly readily differentiated from one another :

(1) Kaolinite group (including halloysite, nacrite, dickite).

(2) Montmorillonite group (including bentonite, beidellite, nontronite).

(3) Mica group.

It has been pointed out* that each group is characterised by a particular large spacing, the approximate value of which is, in the case of—

(1) the kaolinite group, 7 A ;

(2) the monmorillonite group, 15 A in the case of air-dried material ;

(3) the mica group, 10 A.

These lines are not subject to confusion by the proximity of any others.

The diffraction pattern of group (1) minerals is largely destroyed by heating to 500° C ; the pattern of group (2) is still present at 500° C (with a modification referred to below) ; and the pattern of group (3) is stable at all temperatures up to 500° C.

From inspection of Table (1) it is apparent that groups (2) and (3) are represented in the soil colloids examined.   Since the soil colloid material had been air-dried (see section IIB) the absence of a line in the region of 15A indicated the absence of any clay mineral of group (2).

In order to establish that the spacing characteristic of the montmorillonite group could be recorded, a sample of bentonite was obtained from the Geology Department of the University of Western Australia.   Its diffraction pattern showed a very strong line at 12·9 A.   As this value indicated that the sample was partly dehydrated, some material was moistened and air-dried. The diffraction pattern then showed a very strong line at 15·1 A.   This reversible behaviour of the montmorillonite lattice was first observed by Hofmann et al.†   The strength of the 15·1 line was such that if only a relatively small quantity of a group (2) mineral were present in the soil samples, the line should be easily detectable above the scattered background.‡

In order to obtain further evidence as to the mineral constituents of the soil colloids, and also with the object of assigning an origin to all our recorded lines, all the observed interplanar spacings as given in Table (1) were compared

*See, for example, Kelley and Dore, Soil Sc. Soc. Proc., 1937, p. 115.

†Zeit. f. Krist., 86, 340, 1933.

‡Since this report has been completed a clay fraction from the Huon Valley in southern Tasmania has been examined. In its diffraction pattern a 15 A line is readily detectable.

with published data relating to pure clay minerals. No data is known for any Australian clay minerals. From this data lists of spacings were drawn up for each of the following three pure minerals representative of the three groups of soil colloids : kaolinite, montmorillonite, and muscovite. Only lines of medium or higher intensity in the X-ray patterns of the pure minerals were included in each list, it being assumed that the faintest lines in the pattern of a pure mineral may not appear, for various reasons, in the pattern of a clay colloid containing the mineral. Since corresponding lines showed differences from observer to observer (both with respect to spacing and with respect to intensity) a mean intensity and a mean spacing were adopted for each line where corresponding lines from observer to observer could be definitely identified. In the drawing up of these lists all the relevant data that appears in the following published works was used : Nagelschmidt (Zeit. f. Krist. 87, 120, 1934) and Favajee (Zeit. f. Krist. 100, 425, 1939). In Table (2) are tabulated the mean interplanar spacings of A 1351. A plus sign in one of the last three columns indicates an agreement (to within 3% in the case of line 1 and to within less than 3% in the case of the remaining lines) between the value of a spacing obtained experimentally for the soil colloids by the authors of this paper and a spacing obtained from published data for one of the three representative minerals.

TABLE (2).

Comparison of A 1351 *with Published Data.*

A 1351			Kaolinite.	Montmoril-lonite.	Muscovite.
Line.	Intensity.	d/n in A.			
1	m	10·29	—	—	+
2	m	7·21	+	—	—
3	v w	5·82	—	—	—
4	v w	4·95	—	+	+
5	v s	4·46	+	+	+
6	v w	4·17	+	—	—
7	m	3·55	+	—	—
8	m	3·32	—	—	+
9	w	3·02	—	+	+
10	w	2·84	—	—	+
11	s	2·56	+	+	+
12	d	2·39	+	—	—
13	v w	2·13	—	—	+
14	v w	1·97	+	—	+
15	v w	1·85	—	—	—
16 / 17	d	1·66	+	+	+
18	s	1·49	+	+	+
19	v w	1·43	—	—	—
20	v w	1·36	—	—	+
21	w	1·29	—	+	+
22	w	1·24	—	—	—

v s = very strong ; s = strong ; m = medium ; w = weak ; v w = very weak ;
d = diffuse.

All the lines listed (from published data as described above) for kaolinite, montmorillonite, and muscovite have been fitted into Table (2), except the strong montmorillonite line at 15 A (the absence of which has already been discussed) and a medium kaolinite line at 2·29 A. This line may be one

of two into which line 13 was doubtfully resolved with Fe radiation, as described in the previous section. It may be seen from the table that whereas no soil colloid line that can be assigned to montmorillonite may not also be assigned to one or both of the other two minerals, there are several instances of soil colloid lines that can only be assigned to one or both of kaolinite and muscovite. These facts provide further evidence in support of the conclusions reached from a consideration of the large characteristic spacings.

Lines 4 and 10 occur in the positions where the β line associated with lines 5 and 11 would fall. Intensity considerations lead to the conclusion that the β line, if present at all, is definitely not the sole contributor to lines 4 and 10.

A plus sign in only one column suggests that the line is characteristic of that particular mineral. This however may not be true for the reason that no account was taken of weak lines when the kaolinite, montmorillonite, and muscovite lists were drawn up.

Four lines have not been assigned any origin. Line 3 has already been discussed. Lines 15, 19, and 22 could have been assigned a possible origin if lines weaker than medium in the lists drawn up from published data had been taken into account. By a similar procedure further origins could have been assigned to lines 20 and 21.

With regard to non-clay constituents of the soil colloids, the possibility of quartz being present cannot be excluded in view of the appearance of a line in the position of the strong quartz line (3·34 A). From the non-appearance of a line at 2·69 A, haematite may be excluded. No opinion could be formed as to the presence or absence of geothite since the strong geothite lines correspond with lines of known different origin. A magnetic test with an electro-magnet revealed no magnetite.

Confirmation of these conclusions was obtained as a result of heat treatment. Some soil colloid material of A 1346 (water dispersed) was kept at about 500° C in air in an electric furnace for three days. The colour changed from greyish-yellow to brownish-yellow. The X-ray diffraction pattern showed a disappearance of line 2 (the characteristic kaolinite line at 7 A) and also of line 7. If weak mica lines are neglected, this line as well as line 2 is characteristic of a group 1 mineral. There appears in the region of line 7 a new line at about 3·72 A. In the absence of line 7 there was some evidence that a weak mica line at 3·48 A was discernable.

It would appear from Table (2) that line 12 should disappear on heat treatment. The line is rather weak and not sharp, and heat treatment has produced in the vicinity a change in the appearance of the pattern that could be explained by the disappearance of line 12 along with the exposure of a doubtful weak line of mica origin.

In the pattern of the heat-treated material line 8 at 3·32 A appeared relatively brighter than in the original pattern. This may be attributed to the appearance of quartz as a result of the destruction of kaolinite.

The pattern that remained after heat treatment (apart from differences just alluded to) was very similar to the original pattern. It is to be assumed that the pattern remaining is due to a mica mineral and that this pattern differs from the colloid pattern listed in Table (2) only in so far as it has been affected by the heat treatment in the manner described above. This pattern, assumed to be the mica pattern, has as its main character (apart from the

10 A line) a pronounced intensity of the 4·46 A line superior to the intensity of any other line. This character seems to differentiate the mica from any of the micas about which published data is available.*

Intensity considerations indicate that the mica mineral is far in excess of the kaolinite mineral in the colloid samples.

Evidence as to the percentage of mica in the clay may be obtained from chemical data. From the analytical data under IIC and on the assumption that the clay contains all the soil potash and that the clay mica here found contains 5% K_2O in which the K is non-replaceable, the clay separation from A 1346 contains 60% mica and that from A 1351 contains 50% mica.

A microscopic examination of the colloid material has been made and results will be published in a separate communication.

VII. SUMMARY.

A technique is described for obtaining X-ray diffraction patterns of crystalline substances (singly or in mixtures) in powdered form, and for deducing interplanar spacings from such patterns. From its application to soil colloid material the crystalline content of colloid separations from two soil samples from the Salmon Gums district in Western Australia designated as A 1346 and A 1351 (representing the subsoil and deep subsoil respectively) has been found to be the same for each sample and to comprise predominantly two clay minerals. One which is in excess belongs to the mica group and resembles illite ; the other belongs to the kaolinite group. Quartz may also be present in small quantity.

A comparison was made between the diffraction patterns obtained from two colloid samples prepared (from the same soil sample) by dispersion in distilled water and by dispersion in caustic soda respectively.

Chemical evidence indicates 60% mica in A 1346 and 50% mica in A 1351.

The results of a microscopic examination will be published in a separate communication.

VIII. ACKNOWLEDGMENTS.

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*An article by Grim and Bradley (Report No. 53, State of Illinois Geological Survey, 1939) has recently come to our notice, in which X-ray data is published for a clay mineral of the illite group with the 10 A line of " medium " (as distinct from " strong ") intensity, agreeing in this respect with our own data.